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The Crystal Structure of γ -Dicalcium Silicate

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Least-squares analysis of three-dimensional single-crystal data confirms that γ -Ca₂SiO₄ is isostructural with olivine, Mg₂SiO₄. The relative positions of the SiO₄ tetrahedra and half the Ca atoms are similar to those in the β and α' forms. The remaining Ca atoms are surrounded by corresponding tetrahedra but considerably displaced. The γ form hydrates less rapidly than the β and α' forms because of the greater strength and uniformity of Ca-O bonding.

Introduction

The polymorphism of dicalcium silicate has been the subject of many investigations because of its importance to portland cement clinker and slag chemistry. Bredig (1950), Nurse (1952), Roy (1958), Smith, Majumdar & Ordway (1961) and others have agreed that four distinct crystalline modifications of Ca₂SiO₄ do exist. These forms, designated α , α' , β , and γ in order of decreasing temperatures of stability, exhibit complex equilibrium phase relations which are still not established beyond doubt. The presently accepted schematic free energy-temperature diagram (Smith, Majumdar & Ordway, 1961) is shown in Fig. 1.

Several authors discuss possible structure types for the various modifications and their interrelations. O'Daniel & Tscheischwili (1942) proposed the olivine-type structure for γ -Ca₂SiO₄ by its analogy with Na₂BeF₄. Greer (1932) apparently reached the same conclusion, from a study of (Ca,Mg)₂SiO₄ solid solutions. The α -Ca₂SiO₄ unit-cell dimensions were deter-

mined by Bredig (1950) and Douglas (1952) from the high temperature X-ray data of Van Valkenburg & McMurdie (1947), by showing an analogy with glaserite, Na₃K(SO₄)₂. The cell dimensions for the α' form, based on analogy with the K₂SO₄ structure, were determined by Bredig (1950) from the data of Trömel and verified by Douglas (1952). Although similarities between the α' and α forms were obvious from a com-

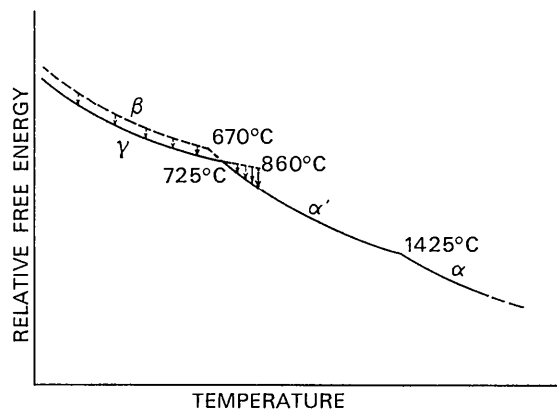


Fig. 1. The schematic free energy-temperature diagram for the polymorphs of Ca₂SiO₄. The solid lines indicate regions of apparent stability; the dotted lines, of apparent metastability.

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parison of the X-ray powder patterns, and the monoclinic unit cell for the β form was known, the β structure was not established until the work of Midgley (1952). Using single crystals of β -Ca₂SiO₄ stabilized with 0.5 wt.% B₂O₃, she determined the atomic arrangement and showed its relationship to the proposed α' structure.

Preparation of single crystals

Single-crystal studies of the high-temperature modifications of "pure" Ca₂SiO₄ have not been made because the phases are not quenchable without additives. The β -Ca₂SiO₄ structure was determined with crystals stabilized with B₂O₃. The high-temperature X-ray powder patterns of the stabilized and unstabilized material are essentially identical, suggesting that the "pure" structure differs little from the stabilized one. The stabilization of the α and α' forms by P₂O₅ has been shown (Nurse, Welch & Gutt, 1959), and the "compound" K₂O.23CaO.12SiO₂ may actually be an example of stabilization by K₂O. No single-crystal studies have yet been reported, however, for the α and α' forms either stabilized or "pure". Single crystals of the γ modification have not been studied heretofore because the large volume expansion of the β - γ transition on cooling usually shatters the crystals into fragments too small for single-crystal X-ray studies.

The single crystals of γ -Ca₂SiO₄ used in this investigation were obtained from preparations of stoichiometric composition 2CaO.SiO₂. Ethyl orthosilicate was hydrolyzed with a calculated amount of Ca(NO₃)₂ solution. The mixture was dried at 100 °C, denitrated at 400 °C, fired to 1000 °C, and finally fired to 1500 °C followed by air quenching. This treatment had been found (Smith, Majumdar & Ordway, 1961) to produce pure γ -Ca₂SiO₄, while slow cooling after firing gave a mixture of γ and β . The resulting sample was mostly pulverized by the 12% volume expansion at the β - γ transformation. The powder was sieved through a 200 mesh screen, and a few single crystals were retained which appeared free of fractures. One of these crystals was used for the structure investigation.

X-ray data and structure calculations

Three-dimensional X-ray data were collected using the Buerger precession camera and Zr-filtered Mo K α radiation. A total of 18 levels along five different directions was used to obtain nearly all the available reflections within the copper sphere. Intensities were estimated visually by comparison with a calibrated intensity scale prepared by timed exposure of a well shaped reflection from the same crystal. The intensities were corrected for the Lorentz and polarization effects, and the resulting values were scaled and combined by the method of Dickerson (1960). Because of the small size of the crystals, no absorption correction was made. A total of 392 independent reflections was obtained.

Precession patterns of single crystals of a natural olivine were also made. Visual comparison of the respective patterns showed the same extinctions and general intensity variations in agreement with O'Daniel & Tscheischwili's hypothesis that the two compounds are isostructural. The crystal axes of the γ -Ca₂SiO₄ were chosen to conform with previous indexings of the powder pattern. Thus, the systematic absences are $h0l$ when $h+l=2n+1$ and $0kl$ when $k=2n+1$ indicating the possible space groups $Pbnm$ or $Pbn2$, which are alternate orientations of the space groups $Pnma$ (No. 62) and $Pna2$ (No. 33) respectively. The former space group was chosen by analogy with the olivine structure as determined by Bragg & Brown (1926) and refined by Belov, Belova, Andrianova & Smirnova (1951) and Hanke & Zemmann (1963). The structure analysis verified the choice. The unit-cell data for γ -Ca₂SiO₄ are listed in Table 1 with those for the other polymorphs. More recent work on olivine by Eliseev (1958) has questioned the accepted space group because of the presence of unindexable powder lines. Belov (Eliseev, 1958) suggested that the extra lines resulted merely from the phenomenon of double reflection, and none of these 'forbidden' intensity maxima was observed in our patterns of olivine or Ca₂SiO₄ where they would be expected, nor were they reported by Hanke & Zemmann (1963). Thus the question raised by Eliseev may be considered settled.

Table 1. Unit-cell data for the dicalcium silicates

Modification	γ	β	α'	α
Crystal system	Orthorhombic	(stabilized*) Monoclinic	(stabilized*) Orthorhombic	Hexagonal
a_0	5.094 ± 0.010 Å	5.48 Å	5.491 Å	5.45 (21.80) Å
b_0	11.371 ± 0.020	6.76	9.248	5.45 (21.80)
c_0	6.782 ± 0.010	9.28	6.790	6.76 (21.54)
Angle		$\beta = 94^\circ 33'$		$\gamma = 120^\circ$
V	392.6 Å ³	342.7 Å ³	344.8 Å ³	173.9 Å ³
Z	4	4	4	2
Space group	$Pbnm$	$P2_1/n$	$Pmcn$	$P\bar{3}m1$
Reference	Present work	Midgley (1952)	Yamaguchi <i>et al.</i> (1957)	Bredig (1950)

* With B₂O₃.

Trial parameters were obtained by adjusting the parameters reported for olivine to accommodate the larger Ca ions replacing Mg ions. These parameters were further improved by hand calculation of a few sensitive structure factors in the $h0l$ and $0kl$ zones. The new parameters, which gave an R value of 0.16 for all

observed reflections, were then refined by the method of least squares, using the Busing & Levy (1959) program on the IBM 704 computer. Four cycles of refinement reduced the R value to 0.10. The resulting parameters are listed in Table 2, with the standard deviations as calculated by the program. The calculated

Table 2. Atomic coordinates for γ -Ca₂SiO₄

Atom	Position	x	Coordinates y	z	Temperature factor B
Ca _I	4(a)	0.000	0.000	0.000	0.79 ± 0.07 Å ⁻²
Ca _{II}	4(c)	-0.0116 ± 0.001 ₂	0.280 ₄ ± 0.000 ₅	0.250	0.68 ± 0.07
Si	4(c)	0.427 ₂ ± 0.001 ₆	0.098 ₅ ± 0.000 ₇	0.250	0.60 ± 0.10
O _I	4(c)	-0.262 ₃ ± 0.003 ₆	0.086 ₇ ± 0.001 ₇	0.250	0.55 ± 0.23
O _{II}	4(c)	0.302 ₀ ± 0.003 ₄	-0.042 ₁ ± 0.001 ₇	0.250	0.48 ± 0.23
O _{III}	8(d)	0.292 ₅ ± 0.002 ₇	0.163 ₃ ± 0.001 ₁	0.059 ₉ ± 0.002 ₂	1.16 ± 0.19

Table 3. Observed and calculated structure factors for γ -Ca₂SiO₄.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
0	0	2	34.9	-26.2	1	4	0	37.7	31.4	2	3	6	5.2	-4.2	3	6	7	7.4	-6.4	
0	0	4	86.5	77.0	3	13.7	8.7	2	4	0	44.8	42.9	9	7.3	5.3	9	7	8.2	-9.1	
0	0	6	28.8	-27.6	4	8.7	8.1	1	26.1	-25.5	3	7	0	38.0	34.3	5	1	0	9.3	
0	2	0	21.8	14.0	5	5.7	4.7	2	16.9	17.4	2	7.7	4.1	1	14.6	14.6	1	14.6	-15.0	
0	2	1	28.8	-20.9	1	5	0	18.4	17.8	4	11.8	10.4	3	7.5	-9.0	2	10.8	12.5		
0	2	2	30.7	26.8	1	19.2	-17.6	5	20.0	-19.9	8	16.2	15.0	4	10.6	10.6	2	20.3	9.7	
0	2	3	6.0	-4.6	2	29.8	25.8	6	6.3	5.7	3	8	0	23.3	21.7	5	9.5	-9.7		
0	2	4	18.7	16.0	3	11.1	10.3	7	8.6	9.3	2	13.2	-12.1	6	11.8	12.7	6	11.8	12.7	
0	2	5	20.0	-17.6	4	15.8	15.2	8	11.6	12.3	4	14.0	13.7	7	13.3	12.6	7	13.3	12.6	
0	2	6	24.3	21.5	5	13.3	-11.8	9	8.4	-7.9	6	13.5	-12.8	8	8.7	7.8	8	8.7	7.8	
0	2	8	12.0	9.8	6	19.1	15.5	2	5	0	9.8	-9.7	8	8.4	-8.8	5	2	0	6.5	
0	4	0	21.8	21.6	7	9.2	6.0	1	11.6	-11.6	3	9	0	24.4	26.4	2	24.4	26.4		
0	4	1	26.2	-23.5	8	11.3	8.9	2	4.8	-2.1	2	24.4	26.4	2	24.4	26.4	2	24.4	26.4	
0	4	2	13.9	13.5	1	6	0	12.1	11.1	3	14.2	13.6	6	22.6	24.2	3	6.2	5.4		
0	4	3	40.9	37.1	1	9.7	-7.9	2	6.2	-7.0	7	8.5	7.7	4	0	0	44.8	42.3	4	5.6
0	4	4	22.9	21.2	2	6.2	-7.0	7	8.5	7.7	4	1	2	33.2	29.7	5	5.7	-3.7	22.0	
0	4	5	13.6	-11.9	3	10.1	-8.7	9	5.7	-5.3	4	1	2	17.1	-18.9	5	3	0	20.3	
0	4	6	16.8	15.7	4	7.0	6.5	2	6	1	17.7	16.2	3	8.3	-8.7	5	3	0	20.3	
0	4	7	19.7	16.9	5	11.3	-7.7	2	24.1	20.2	4	8.9	11.4	4	8.9	11.4	4	8.9	11.4	
0	4	8	16.8	14.8	1	7	0	44.7	44.7	3	17.8	-15.9	6	6.1	-7.0	8	5.6	6.3	15.5	
0	4	9	11.8	-11.6	1	10.5	-9.3	4	6.4	7.1	7	5.3	-4.2	5	4	1	5.8	7.8	6.4	
0	6	0	9.9	7.9	2	10.0	-6.8	5	12.7	11.6	8	9.7	10.0	10.0	5	5	5	5.4	6.4	
0	6	1	42.4	40.7	3	12.7	11.1	6	23.9	21.9	4	2	1	4.0	26.4	4	6.8	-12.1	14.9	
0	6	2	63.2	62.1	4	35.5	35.6	7	11.4	-10.2	2	25.1	26.4	4	12.2	13.7	2	13.7	13.7	
0	6	3	31.3	-32.1	5	7.1	-6.0	8	9.2	8.0	3	7.0	-8.1	2	21.7	25.7	2	21.7	25.7	
0	6	4	27.6	26.7	7	10.0	5.9	9	8.3	7.7	6	21.1	20.6	4	4.9	-3.0	4	4.9	-3.0	
0	6	6	28.7	27.1	8	26.5	22.7	2	7	0	8.4	-9.5	4	3	0	9.9	12.6	5	12.2	
0	6	7	17.0	-19.2	1	8	0	15.2	-13.1	2	15.8	16.2	2	10.3	-12.7	6	21.7	21.5	18.8	
0	6	8	6.7	-7.8	8	10.0	6.8	3	5.7	4.2	7	7.4	3.8	1	9.4	-12.1	1	9.4	-12.1	
0	8	0	15.3	13.5	1	9	0	5.3	-5.2	4	9.9	-10.9	4	8.3	10.4	5	7	0	15.5	
0	8	1	15.2	16.1	1	7.6	-6.4	3	0	1	11.4	-10.0	6	7.2	-7.9	4	16.5	19.1	15.5	
0	8	2	12.9	-13.2	2	40.4	40.4	3	19.9	19.3	8	5.9	6.2	5	8.5	5.8	5	8.5	5.8	
0	8	4	15.5	13.9	3	8.4	6.2	5	5.2	-4.7	4	4	0	22.1	24.9	8	19.3	15.5	6.2	
0	8	6	13.6	13.4	4	7.1	-6.4	7	7	5	10.4	8.9	1	7.6	-24.9	5	8	0	7.3	
0	8	8	11.7	10.3	4	26.6	26.6	9	5.7	-5.5	3	9.3	12.7	7	7.6	-7.8	6	7.8	-6.2	
0	10	0	25.9	26.1	1	10	0	8.0	4.0	3	1	0	24.9	28.6	4	20.0	22.4	4	6.8	
0	10	1	23.4	23.9	1	6.4	4.1	1	19.9	-21.4	5	6.0	-6.4	6	6.4	5.5	2	7.6	-7.8	
0	10	2	6.3	-4.8	5	7.6	4.6	2	23.4	22.8	7	6.5	7.8	8	3.9	4.5	4	4.5	4.5	
0	10	3	15.0	-14.5	1	11	0	18.2	17.7	3	8.2	9.3	4	5	0	15.5	14.7	5	10.2	
0	10	4	25.5	26.0	1	6.8	-3.2	4	15.3	16.5	1	16.5	-18.4	2	19.7	17.1	2	19.7	17.1	
0	10	5	20.9	20.1	2	10.4	8.2	5	16.7	16.7	3	10.9	13.4	3	4	5.5	3	4	5.5	
0	10	7	10.9	-11.9	4	16.5	15.7	6	13.2	11.4	4	7.6	6.8	5	11	0	20.5	21.5	21.5	
0	12	0	12.2	14.1	5	7.0	-3.4	7	7.2	8.2	5	13.3	-14.8	1	8.7	-9.0	1	8.7	-9.0	
0	12	1	16.7	-19.3	6	8.7	6.1	8	7.2	8.0	6	7.1	-7.7	6	0	0	14.2	12.3	12.3	
0	12	2	19.6	21.0	8	13.2	11.6	9	8.0	-7.2	7	9.5	9.6	2	12.2	9.9	2	12.2	9.9	
0	12	3	18.6	19.5	1	12	3	9.2	-8.6	10	15.5	-16.0	9	9.1	-7.5	4	12.5	11.0	11.0	
0	12	4	6.0	6.9	1	13	1	19.1	17.9	1	8.6	-10.5	4	6	0	10.5	6	1	0	8.5
0	12	5	11.3	-14.6	2	16.0	15.0	2	26.7	28.6	2	13.9	12.9	1	5.5	4.4	1	5.5	4.4	
0	12	6	10.7	10.7	3	16.0	-15.5	4	15.3	-18.4	2	21.4	23.1	4	4.9	4.8	4	4.9	4.8	
0	14	0	10.9	11.6	5	15.6	14.8	5	8.3	-8.6	3	12.0	-11.3	5	5.7	4.6	5	5.7	4.6	
0	14	1	5.4	-6.9	6	16.1	12.7	6	11.9	-11.9	4	6.5	6.0	6	5.0	-5.7	6	5.0	-5.7	
0	14	2	5.9	7.4	7	13.7	-11.3	7	12.2	-13.2	5	12.0	10.3	6	2	1	13.6	14.3	14.3	
1	0	1	20.3	-15.7	1	14	0	7.8	-5.8	1	22.0	21.8	6	13.9	6	2	21.8	22.7	22.7	
1	0	3	12.4	-10.8	8	5.3	4.2	3	0	1	9.2	-8.3	7	9.2	-8.3	1	14.4	-13.4	-13.4	
1	0	5	16.7	-14.3	1	15	0	20.3	20.4	4	20.4	-19.5	4	7	0	11.9	-12.3	5	10.9	11.4
1	1	1	22.4	-19.9	4	16.3	17.0	6	7.2	5.6	6	6.4	6.8	6	3	0	8.3	8.3	-4.1	
1	1	2	54.5	49.8	2	0	0	27.3	28.0	7	12.5	-12.1	1	8.7	-11.8	3	8.1	-7.6	-7.6	
1	1	3	22.9	19.8	4	5.3	-4.8	8	20.8	19.8	2	9.8	9.8	4	13.8	12.3	4	13.8	12.3	
1	1	4	4.3	2.8	4	35.6	34.7	7	11.5	9.3	3	5.9	7.8	7	5.5	2.2	7	5.5	2.2	
1	1	5	8.9	-8.4	8	27.6	25.0	3	4	0	21.9	-21.6	4	8.6	9.3	6	4	0	22.3	
1	1	6	30.5	28.9	8	23.0	18.9	1	19.3	17.8	5	8.2	-10.7	4	20.2	22.7	4	20.2	22.7	
1	1	7	9.9	8.5	1	20.3	17.4	2	10.6	8.8	6	9.5	10.9	6	6	0	14.6	14.6	14.6	
1	1	9	6.6	-6.5	3	9.9	-9.9	3	11.1	9.8	3	11.5	9.5	0	-10.5	12.3	3	11.5	9.5	
1	2	0	17.5	-14.2	4	8.7	8.1	4	11.7	4	11.7	4	6.7	7.7	6	8	1	14.7	-16.2	
1	2	1	8.3	-5.2	4	8.7	8.1	4	11.7	4	11.7	4	6.7	7.7	6	8	1	14.7	-16.2	
1	2	2	25.0	-20.3	5	13.6	12.4	5	11.2	11.1	5	7.5	7.8	2	7.7	9.8	2	7.7	9.8	
1	2	3	16.4	14.3	6	8.9	-8.1	6	11.3	10.3	4	10	0	14.8	12.4	7	1	0	19.6	
1	2	4	5.8	5.0	7	6.5	-6.6	7	11.2	-11.4	1	14.9	13.5	5	6.9	6.9	1	15.0	-13.5	
1	2	5	5.7	4.7	9	6.1	-6.1	9	9.9	8.1	2	5.9	6.9	2	5.9	6.9	2	5.9	6.9	
1	2	7	42.1	38.4	2	2	-1	11.1	9.8	3	11.1	9.8	3	11.5	-10.5	3	11.5	-10.5	10.5	
1	2	8	16.9	13.7	2	60.6	58.1	2	29.8	30.5	4	13.8	12.3	4	13.8	12.3	4	13.8	12.3	
1	2	9	32.6	-32.																

structure factors are listed beside the corresponding observed values in Table 3.

A three-dimensional electron density map was calculated using all the measured structure amplitudes with the signs determined from the final least-squares

refinement. The electron density distribution around each atomic position is essentially spherical implying that the assumption of isotropic thermal motion is good. A ring of peaks approximately one $e.\text{\AA}^{-3}$ in height around each calcium may be due to the termination of

Table 4. *Interatomic distances in olivine-type (R_2MO_4) compounds whose structures are accurately known.*

Compound	γ -Ca ₂ SiO ₄	Mg ₂ SiO ₄	(Fe,Mg) ₂ SiO ₄	Fe ₂ SiO ₄	Al ₂ BeO ₄	
R =	Ca	Mg	(Fe,Mg)	Fe	Al	
M =	Si	Si	Si	Si	Be	
Distance	Multiplicity					
(R_I octahedron)						
R _I —O _I	2	2.373 ^o \AA	2.087 ^o \AA	2.097 ^o \AA	2.122 ^o \AA	1.859 ^o \AA
R _I —O _{II}	2	2.338	2.070	2.103	2.127	1.896
R _I —O _{III}	2	2.419	2.141	2.187	2.230	1.914
O _I —O _{II} *	2	3.224	2.840	2.867	2.902	2.551
O _I —O _{II}	2	3.435	3.035	3.069	3.103	2.755
O _I —O _{III} *	2	3.222	2.845	2.886	2.919	2.528
O _I —O _{III}	2	3.548	3.128	3.167	3.229	2.800
O _{II} —O _{III} **	2	2.674	2.529	2.562	2.555	2.511
O _{II} —O _{III}	2	3.936	3.368	3.441	3.531	2.866
(R_{II} octahedron)						
R _{II} —O _I	1	2.537	2.173	2.200	2.236	1.944
R _{II} —O _{II}	1	2.289	2.071	2.092	2.126	1.857
R _{II} —O _{III}	2	2.407	2.076	2.062	2.086	1.895
R _{II} —O _{III}	2	2.413	2.220	2.271	2.286	2.016
O _I —O _{III} *	2	3.222	2.845	2.866	2.919	2.528
O _I —O _{III}	2	3.537	3.036	3.064	3.097	2.743
O _{II} —O _{III}	2	3.258	2.945	2.937	2.971	2.740
O _{II} —O _{III}	2	3.615	3.211	3.267	3.327	2.845
O _{III} —O _{III} **	1	2.577	2.562	2.609	2.586	2.552
O _{III} —O _{III}	1	4.205	3.430	3.441	3.514	2.924
O _{III} —O _{III}	2	3.312	3.004	3.016	3.038	2.759
(M tetrahedron)						
M —O _I	1	1.589	1.629	1.638	1.624	1.580
M —O _{II}	1	1.725	1.635	1.648	1.649	1.688
M —O _{III}	2	1.637	1.618	1.637	1.632	1.631
O _I —O _{II}	1	2.661	2.741	2.739	2.719	2.772
O _I —O _{III}	2	2.754	2.752	2.774	2.771	2.765
O _{II} —O _{III} **	2	2.674	2.529	2.562	2.555	2.511
O _{III} —O _{III} **	1	2.577	2.562	2.609	2.586	2.552
(Average Values)						
R _I —O		2.383	2.099	2.129	2.160	1.890
R _{II} —O		2.411	2.139	2.126	2.184	1.937
R —O		2.397	2.119	2.128	2.172	1.914
M —O		1.644	1.625	1.640	1.634	1.622
O—O (R unshared)		3.566	3.126	3.164	3.207	2.796
O—O (R—R shared)		3.223	2.842	2.877	2.910	2.540
O—O (R—M shared)		2.625	2.545	2.578	2.570	2.532
O—O (M unshared)		2.707	2.756	2.762	2.745	2.769
Reference	Present work	Gibbs, Moore, & Smith (1963)	Gibbs, Moore, & Smith (1963)	Hanke (Smith, 1963)	Farrell, Fang, & Newnham (1963)	

*O—O distance shared by two octahedra

**O—O distance shared by one tetrahedron and one octahedron

the data at the copper sphere. The remainder of the background shows no significant density. The omission of an absorption correction is supported by the low background.

Discussion of the structure

Table 4 lists the interatomic distances found in γ -Ca₂SiO₄ and other olivine-type compounds whose structures are accurately known. The structure of Al₂BeO₄ was reported by Farrell, Fang & Newnham (1963). The Mg₂SiO₄ structure was determined by Hanke & Zemmann (1963) and verified by Gibbs, Moore & Smith (1963), who also give the structure of (Fe_{0.50}Mg_{0.50})₂SiO₄. The Fe₂SiO₄ structure was determined by Hanke (Smith, 1963). Table 5 lists the corresponding bond angles for each of the olivine-type compounds.

For γ -Ca₂SiO₄ the SiO₄ tetrahedron is surprisingly irregular. The Si-O_I distance is unusually short and the Si-O_{II} distance unusually long when compared with those in SiO₄ tetrahedra of other well determined silicate structures. Compilations of Si-O distances (*International Tables for X-ray Crystallography*, 1962; Smith & Bailey, 1963) do not indicate any other structure with such a large variation. The average Si-O distance

of 1.644 Å however, is close to the values of 1.62 to 1.63 Å reported in the compilations.

Among the olivine-type compounds shown in Tables 4 and 5 only Al₂BeO₄ shows a similar relation among the interatomic distances in the tetrahedron. Its Be-O distances do show the same large deviations and there are even larger variations in angle. These deviations are apparently not due to experimental error, and probably are distortions in the hexagonal close packing of oxygen atoms developed by the sharing of some pairs of oxygen atoms between adjacent coordination polyhedra.

Neither of the octahedral configurations can be considered regular. No large deviations in distances are evident, but the angles depart significantly from 90°. It is interesting to note in Table 5 the similarity of all the corresponding angles in the olivine-type structures. The trends from γ -Ca₂SiO₄ to Al₂BeO₄ reflect the size of the cations and their effects on the distortions of the oxygen packing.

The oxygen-oxygen distances in Table 4 can be divided into four categories, those in octahedra not shared with any other oxygen polyhedron, those shared between two octahedra, those shared between an octahedron and a tetrahedron, and those in tetrahedra which are unshared. Distances in the last two cate-

Table 5. Bond angles in olivine-type (R₂MO₄) compounds whose structures are accurately known.

Compound		γ -Ca ₂ SiO ₄	Mg ₂ SiO ₄	(Fe,Mg) ₂ SiO ₄	Fe ₂ SiO ₄	Al ₂ BeO ₄
R =		Ca	Mg	(Fe,Mg)	Fe	Al
M =		Si	Si	Si	Si	Be
Angle	Multiplicity					
(R _I octahedron)						
O _I -R _I -O _{II}	2	86°	86°	86°	86°	86°
O _I -R _I -O _{II}	2	94	94	94	94	94
O _I -R _I -O _{III}	2	84	85	85	84	84
O _I -R _I -O _{III}	2	96	95	95	96	96
O _{II} -R _I -O _{III}	2	68	74	73	71	82
O _{II} -R _I -O _{III}	2	112	106	106	108	98
(R _{II} octahedron)						
O _I -R _{II} -O _{III}	2	81°	81°	80°	80°	79°
O _I -R _{II} -O _{III}	2	91	91	92	91	91
O _{II} -R _{II} -O _{III}	2	101	97	97	98	94
O _{II} -R _{II} -O _{III}	2	88	91	90	90	94
O _{III} -R _{II} -O _{III}	1	65	71	70	69	79
O _{III} -R _{II} -O _{IH}	2	87	89	88	88	90
O _{III} -R _{II} -O _{III}	1	121	111	113	115	101
(M tetrahedron)						
O _I -M-O _{II}	1	107°	114°	113°	112°	116°
O _I -M-O _{III}	2	117	116	116	117	119
O _{II} -M-O _{III}	2	105	102	102	102	98
O _{III} -M-O _{III}	1	104	105	106	105	103
Reference		Present work	Gibbs, Moore, & Smith (1963)	Gibbs, Moore, & Smith (1963)	Hanke (Smith, 1963)	Farrell, Fang, & Newnham (1963)

gies depend only on the tetrahedral cation and on the minimum oxygen–oxygen approach, and are essentially the same in all the structures including Al_2BeO_4 . Distances in the first two categories depend on the octahedral cation and show the largest values around the large Ca ion and the smallest around the Al ion.

In the AlO_6 groups the oxygen atoms are essentially in contact and consequently show the same range of distances as found in the tetrahedra. This identity caused Farrell, Fang, & Newnham (1963) to divide the oxygen–oxygen distances of Al_2BeO_4 into only two groups. This division shows, however, that the sharing of oxygen pairs by more than one cation does indeed distort the arrangement, even in the structure whose oxygen packing is most nearly ideal.

Crystal chemistry of the polymorphic forms of Ca_2SiO_4

The structural similarities and differences of the various polymorphic forms of Ca_2SiO_4 help to explain their relative reactivities as well as the kinetics of the phase transitions. Fig. 1 indicates the sequence of transformations on heating. The α' form develops sluggishly between 725 °C and 860 °C. Further heating above 1425 °C causes rapid inversion to the α phase. No further polymorphic changes have been detected up to the melting point. Cooling causes the sample to revert to the α' modification at 1421 °C. Thus the α – α' inversion shows a very small hysteresis. With continued cooling a β form appears at 670 °C. The γ modification appears only when the temperature drops below 500 °C. However, the β – γ transition is variable. Under some conditions the transition is rapid and essentially complete, whereas under other conditions it may not go to completion even with cooling to liquid nitrogen temperatures. The reversibility of the β – α' inversion is demonstrated by the rapid transformation to the α' phase on reheating the β form to 675 °C.

Fig. 2 shows corresponding projections of the four structures. The α' and β structures differ primarily in the shape of the unit cell. A strong similarity does exist; the transformation is very nearly displacive in the terminology of Buerger (1948). The coordination of the Ca in α' - Ca_2SiO_4 is eightfold. In the β form, the coordination number of one Ca is eight, and that of the other is between six and nine, judging from the data of Midgley (1952) and McIver (1962). The transformation involves rotation of the SiO_4 tetrahedra accompanied by the breaking of very few Ca–O bonds, and might be expected to take place very rapidly.

The relationship of the γ structure to the β and α' structures is of interest. Although the γ structure has been considered by many to be significantly different from the β and α' forms, study of the three-dimensional models does reveal some similarities in general arrangement of atoms. The relative positions in the two structures are the same for SiO_4 tetrahedra and one set of Ca atoms. The other set of Ca atoms is dis-

placed, but still related to the same SiO_4 tetrahedra. The lower (sixfold) coordination of the Ca explains the larger molecular volume of the low-temperature phase. Both the γ – α' and the β – γ phase changes involve a change in coordination of the Ca accompanied by a rotation of the SiO_4 tetrahedra and must be considered as semi-reconstructive. The sluggish nature of these transformations may be due to the complexity of the bond readjustments. The likelihood of breakup of a single crystal into a powder when passing through either transformation is obvious. The close similarity of the β and α' structures helps to explain why the β form, rather than the apparently more stable γ form, develops from the α' form on cooling.

Of the four structures, the glaserite model for the α structure is the most doubtful. Good X-ray patterns of the pure α - Ca_2SiO_4 have been difficult to obtain. Yamaguchi, Miyabe, Amano & Komatsu (1957) report patterns which were obtained with a high-temperature diffractometer. They find that the glaserite lattice does not explain the pattern unless the a axis is multiplied by four and the c axis by three. If their findings are true, the structure is more complex than heretofore accepted. Thus, it is not possible to discuss the structural changes at the α – α' inversion with any certainty at this time. However, assuming the glaserite model is reasonably close to the true structure, it can be seen in Fig. 2 that half the SiO_4 tetrahedra must be rotated so that apices point in opposite directions at the phase change. The rapidity of this transformation is certainly facilitated by the elevated temperature even though the change may require a structural rearrangement.

The effect of crystal structure of the various forms of Ca_2SiO_4 on their rates of hydration will be completely understood only when the mechanism of hydration is fully known. It seems clear that the hydration process is complex and involves several stages. Which of these stages control the hydration rate is yet to be established.

The initial stage undoubtedly involves the attachment of hydrogen ions to the oxide structure and their migration into the interior of the crystallite. In the aqueous phase the hydrogen ions are continually transferred from one oxygen to another, and some may attach themselves to the oxygens at the surface of the crystal. Transfer to other oxygens deeper in the crystal may occur, with decreasing frequency. The formation of OH^- groups weakens the electrostatic forces holding these oxygens to the calciums. This weakening of forces allows the structure to open up and enhances the inward migration. The small size of a hydrogen ion also facilitates its migration; it is doubtful that a hydroxyl or hydronium ion or a water molecule could diffuse as rapidly into the unexpanded structure.

The likelihood of proton diffusion in the hydration of calcium silicates is suggested by the evidence that hydrogen is ubiquitous in quartz (Brunner, Wondratschek & Lawes, 1961), rutile (Soffer, 1961), fused silica (Adams & Douglas, 1959), and silicate glasses (Scholze,

1959). In all these materials hydrogen has been shown by infrared spectra to exist as OH groups; but the nature (Dole, 1941; Hubbard, 1946, Hubbard & Rynders, 1947; Rynders, Grauer & Hubbard, 1948; Hubbard, Cleek & Rynders, 1950; Hubbard, Black & Rynders, 1950; Hubbard, Black, Holley & Rynders, 1951; Hubbard & Cleek, 1952) and rapidity (Beck & Wynne-Jones, 1952) of the proton response of glasses as membranes in pH electrodes, and the fact that hydrogen passes by electrolysis through α -quartz like other cations (Kats & Haven, 1960) argue for the independent migration of protons. The diffusion of protons in metals was shown much earlier (Coehn, 1929),

and diffusion of hydrogen into steel has been found to result from contact between the metal and liquid water (Norton, 1940). Inasmuch as the diffusion of protons may be hindered by the absence of a mechanism for charge compensation in the bulk of the solid, their major effect in calcium silicate hydration may occur within a few unit cells of the surface.

The hydrated phase might develop in two possible ways. The anhydrous crystallite might be attacked only at the surface with the structural units, whose release is initiated by the hydrogen ions, splitting off and re-joining to form hydrated compounds until the anhydrous crystallite is replaced by many smaller hydrate

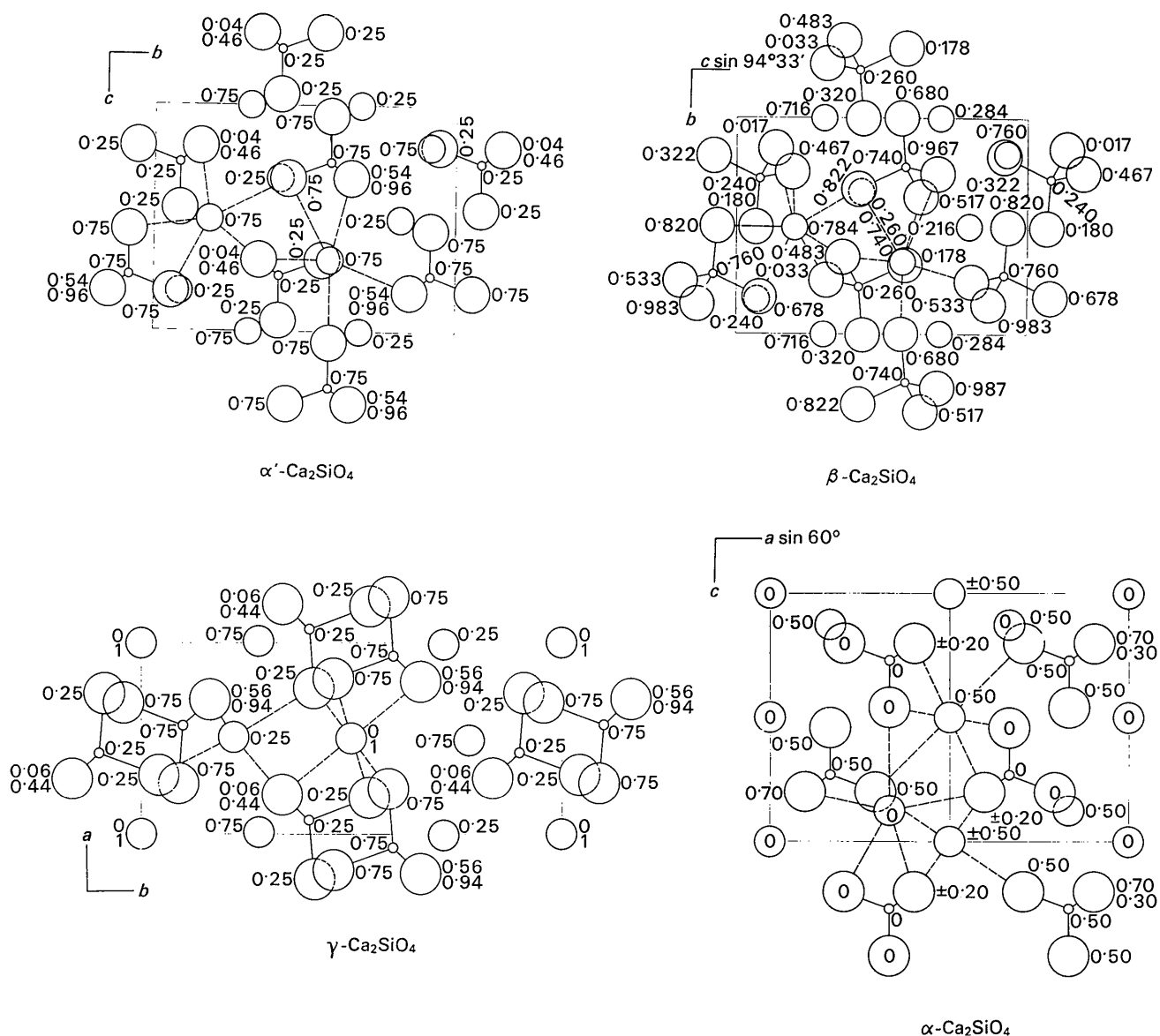


Fig. 2. Related projections of the four Ca_2SiO_4 polymorphs. The small circles represent the silicon atoms, the large ones the oxygen atoms and the intermediate circles the calcium atoms. The coordinate listed with each atom is the fraction of the unit-cell repeat normal to the plane of the projection. The solid lines indicate the Si-O bonds, and the dashed lines indicate the Ca-O bonds around some of the calcium atoms.

crystallites. Alternatively, the hydrogen ions migrating into the crystallite might cause structural rearrangement to permit the entrance of hydroxyl ions and eventual replacement of the original anhydrous crystallite by a single hydrated crystallite. The second type of process occurs only when the structure of the reaction product is similar to that of the original crystal and the volume change is not large.

The crystal structures of the calcium silicate hydrates are incompletely known, but appear in general to contain isolated SiO_4 tetrahedra or chains in which some of the oxygens are replaced by hydroxyl groups. The formation of these groups from the anhydrous calcium silicate requires the splitting of many if not all the Ca–O bonds. Hydrogen ions attaching themselves to the released SiO_4 groups form the silicate ions which then recombine with Ca^{2+} to form the hydrated compound. The structural rearrangement and volume change suggest the splitting process as the most likely mechanism, and the literature on applications of electron microscopy to the hydration problem gives no indication that the crystals of the hydration products form pseudomorphs of the original anhydrous crystallites.

The initial form of the silica in solution is probably a monosilicate ion, in as much as the SiO_4 tetrahedra are not linked in the Ca_2SiO_4 crystal. The tendency for the linkage or independence of silicate groups to be preserved during solution is illustrated by Murata (1946) and Schlecht (1946). The monosilicate ions would polymerize in solution (Iler, 1955) but for the high concentration of calcium ions produced simultaneously. Apparently the calcium silicate hydrate (I) (Greenberg, 1954) forms before any substantial polymerization can take place.

In solutions of low pH, all forms of Ca_2SiO_4 are readily soluble. The hydration of Ca_2SiO_4 in cement, however, takes place at the relatively high pH of a saturated $\text{Ca}(\text{OH})_2$ solution. At this low hydronium ion concentration any differences in the effectiveness of the hydrogen ions in opening up the various oxide structures should be more marked. Lerch & Bogue (1927) show that the rates of hydration are considerably higher for the β modification than for the γ form under identical conditions. Although this rate could be influenced somewhat by the rate of nucleation and growth of the hydrated species, the species is in general identical regardless of the initial Ca_2SiO_4 modification. Thus the difference in hydration rates is probably a reflection of the crystallographic differences of the starting phases. Inasmuch as hydration involves splitting of the Ca–O bonds, it is logical to relate the differences in reactivity to differences in Ca–O bonding, although the strength of Ca–O bonds to any one oxygen atom also affects the Si–O bond of that oxygen atom.

It is helpful to compare the coordination polyhedra in the Ca_2SiO_4 modifications. In γ - Ca_2SiO_4 the Ca ions are all octahedrally coordinated, whereas in β - Ca_2SiO_4 the coordination is 7 or 8. Pauling's (1960) rule re-

quires the total strength of bonds around an ion to be equal to its formal charge. For oxygen, this total would be two units, one of which is allocated to an Si–O bond. The other unit of bond strength, consequently, is distributed among the n Ca ions to which the oxygen is coordinated. The average strength of each bond is then $1/n$. In γ - Ca_2SiO_4 n equals 3 and each bond has a strength of $\frac{1}{3}$. In β - Ca_2SiO_4 n equals 3 or 4 and the strength of some Ca–O bonds is less than in the γ form. Thus a hydrogen ion is more likely to split a Ca–O bond in the β modification. Moreover, the β form has rather irregular Ca coordination polyhedra. The longer bonds are even weaker than the average, and although the deviations in length are small they may be significant with respect to the effectiveness of the hydrogen ions in splitting the bond.

The metastability of the β phase also has an influence on the hydration. Its tendency to undergo a catastrophic structural rearrangement may greatly increase the local effectiveness of a hydrogen ion in opening up the structure to further reaction, even if the rearrangement is inhibited from spreading throughout the crystal by the presence of stabilizing impurities. The complexity of the hydration processes indicates that much is yet to be learned about the relationships of these processes to the crystal structures of the unhydrated phases.

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The Crystal Structure of Tetragonal Selenium Trioxide

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The crystal structure of selenium trioxide has been determined by three-dimensional Fourier synthesis followed by least-squares refinement. The tetragonal unit cell ($P4_21c$, $a=b=9.636$, $c=5.28$ Å) contains two $(\text{SeO}_3)_4$ ring molecules, situated at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, their $\bar{4}$ axes coinciding with those of the cell. The average Se-O distances are 1.77 and 1.55 Å from Se to bridging and non-bridging O.

Introduction

Lehmann & Krueger (1952) described a method for the preparation of selenium trioxide in gram quantities by the action of sulphur trioxide on potassium selenate. A liquid mixture of sulphur trioxide and selenium trioxide results. Pure selenium trioxide can be obtained by distilling off the much more volatile sulphur compound. Thermal analysis of the SeO_3 - SO_3 system (Mijlhoff & Gerding, 1963) revealed that mixed crystals are formed having a composition between 25 and 100 mole % SeO_3 . An X-ray analysis was carried out in order to determine the constitution of the solid selenium trioxide and of the mixed crystals.

Experimental

Mixed crystals were obtained by slow crystallization from a liquid mixture, and pure selenium trioxide crystals by slow sublimation in high vacuum. The oxides are very hygroscopic and chemically active,

but it was possible to select suitable crystals from a sample immersed in a commercial liquid Freon. Unit-cell dimensions were estimated from Weissenberg photographs containing aluminum powder calibration lines. Systematic absences determined the space group uniquely. Crystal data are collected in Table 1. The mixed crystal consisted of two fragments differing slightly in cell volume, probably because they had different sulphur trioxide contents.

Table 1. *Crystal data*

SeO_3 crystal	$a=b=9.636 \pm 0.0003$, $c=5.28 \pm 0.02$ Å.
SeO_3 - SO_3 mixed crystal	$a=b=9.486-9.413$, $c \approx 5.12$ Å.
Space group: $P4_21c$	

Intensities were obtained from integrated equi-inclination Weissenberg photographs made with $\text{Cu K}\alpha$ radiation by the multiple film technique, the crystal rotating about the c (needle) axis. The zero to fourth level intensities for the pure selenium trioxide crystal were scaled by comparison with $h0l$ intensities derived from a precession photograph made with $\text{Mo K}\alpha$

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